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<p>(21) International Application Number: PCT/GB94/01654 (22) International Filing Date: 29 July 1994 (29.07.94) (30) Priority Data: 9315771.7 30 July 1993 (30.07.93) GB (71) Applicant (for all designated States except US): EPICHEM LIMITED [GB/GB]; Power Road, Bromborough, Wirral, Merseyside L62 1TZ (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): JONES, Anthony, Copeland [GB/GB]; Rose Tree Cottage, Georgian Close, Eccleston Park, Prescott L35 7JW (GB). (74) Agent: ROYSTONS; Tower Building, Water Street, Liverpool L3 1BA (GB).</p>		<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: METHOD OF DEPOSITING THIN GROUP IIIA METAL FILMS (57) Abstract A method of depositing a Group IIIA metal layer of high purity on a substrate comprises pyrolyzing contacting the substrate with a tritertiary butyl compound of the Group IIIA metal and pyrolyzing the compound to leave the Group IIIA metal deposited on the substrate. The method of the invention may be used on any suitable substrate, such as silicon or polyimide. The method of the invention may be used for the growth of Group IIIA/silicon alloys as well as for depositing semi-conducting III-V alloys such as, for example, AlGaAs, AlInAs and AlSb.</p>		

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TITLE: Method of depositing thin Group III A metal films.

DESCRIPTION

This invention concerns a method of depositing thin metal films, particularly of aluminium.

5 The deposition of thin films of aluminium is important for a variety of applications, such as the metallisation of silicon devices in VLSI technology, the growth of semi-conducting III-V alloys eg. AlGaAs, AlInAs and AlSb and the growth of dielectrics, such as
10 AlN. In addition, hybrid sensors based on digital recording media are currently under development which require the deposition of aluminium on micron-size steps or holes etched on silicon.

 Metalorganic chemical vapour deposition (MOCVD)
15 is an attractive thin film growth technique possessing the advantages of large area growth capability, accurate control of layer thickness and good conformal step coverage. Much effort has, therefore, been directed at developing suitable aluminium CVD precursors.

20 Volatile metalorganic compounds of aluminium have been widely investigated as CVD precursors including trimethylaluminium, dimethylaluminium hydride and higher aluminium alkyls of the formula AlR_3 where R is n-propyl, n-butyl and i-butyl. However, aluminium films

grown using these precursors have frequently demonstrated poor morphology and low purity. In particular, carbon contamination has resulted from the decomposition of the organic radical during metalorganic
5 pyrolysis. That has stimulated research into the aluminium hydride based adducts bis-trimethylamine alane and dimethylethylamine alane from which carbon free aluminium and low carbon content AlGaAs have been grown. However, doubts remain about the large scale application
10 of these alane adducts due to an unpredictable gas phase chemistry which can lead to premature decomposition and also their tendency to liberate hydrogen during storage at room temperatures.

The most successful and widely investigated CVD
15 precursor to date has been triisobutylaluminium (TIBA). Detailed surface science studies have shown that at temperatures less than 327°C the facile β -hydride elimination of iso-butylene leads to carbon free aluminium films. However, at higher temperatures the
20 iso butyl radical can eliminate a β -methyl group which leads to surface methyl radicals and to a significant increase in carbon content of the deposited aluminium film. That limits the temperature range for aluminium
25 deposition from TIBA and precludes its use in the growth of technologically important Al/Si alloys, which require high substrate temperatures, typically above 400°C, to

pyrolyze the silicon precursor, typically SiH_4 .

Therefore, a need exists for an aluminium precursor which combines the advantages of stability associated with trialkylaluminium compounds with the
5 potential to deposit high purity aluminium films. Analogous Group IIIA metal compounds may also be useful for their deposition.

It has now been surprisingly found that tritertiarybutyl aluminium may be used as a precursor
10 for aluminium deposition.

Accordingly the present invention provides a method of depositing a Group IIIA metal film on a substrate comprising the steps of contacting the substrate with a Group IIIA metal precursor and treating
15 the precursor to decompose leaving the Group IIIA metal deposited on the substrate, wherein the precursor is the tritertiarybutyl compound of the Group IIIA metal.

The present invention further provides a substrate having a Group IIIA metal layer deposited
20 thereon from a precursory decomposing same on the substrate, wherein the precursor is a tritertiary butyl compound of the Group IIIA.

The Group IIIA metals of importance for the method of the invention are aluminium, gallium, and
25 indium, of which aluminium is of most importance.

In a preferred method of the invention the

precursor is delivered to a substrate as a vapour phase and is pyrolyzed on the substrate to leave a film of metal on the substrate. The method of the invention may also be carried out in the liquid phase, such as, for example, by coating the substrate with the precursor or by dipping the substrate into the precursor, before heating to pyrolyze the precursor to leave the metal on the substrate.

In a preferred method of the invention the substrate is heated to a suitable temperature to pyrolyze the precursor. Temperatures in the range of 150°C to 400°C may be suitable, although temperatures above and below this range may also be used.

The method of the invention may be used on any suitable substrate, such as silicon or polyimide. The method of the invention may be used for the growth of Group IIIA/silicon alloys, especially aluminium silicon alloys, which require very high temperatures to pyrolyze the silicon precursor, typically SiH_4 .

The method of the invention may be used for despositing semi-conducting III-V alloys such as, for example, AlGaAs, AlInAs and AlSb and for the growth of dielectrics, such as AlN.

Tritertiarybutyl aluminium (TTBA) may also be a suitable precursor for growth of low carbon AlGaAs by reduced pressure MOVPE or by chemical beam epitaxy

(CBE), in which methyl-free metalorganic precursors have been shown to be essential.

Tritertiarybutyl aluminium may extend the temperature range from which high purity aluminium can be deposited. TTBA may be used in a range of applications in the growth of conductive thin films of aluminium using LPCVD.

This invention will now be further described by means of the following Example

10 Example

Tritertiarybutyl aluminium was synthesised using the method described in Ann. Chem. 719 (1968)40 and the resultant colourless liquid was characterised using proton nuclear magnetic resonance (^1H NMR) and inductively coupled plasma emission spectroscopy (ICP-ES)

^1H NMR (C_6D_6) ppm : 1.3 (s, $\text{Al}-\text{C}(\text{CH}_3)_3$)

ICP-ES: Al content (%) found 13.1, calculated 13.6.

20 Aluminium films were deposited in a simple cold wall horizontal quartz reactor (Electrogas Ltd) using radiant substrate heating. The substrates used were Si (111) single crystal slices which were degreased using acetone, washed in 20% HNO_3 /DI water and dried before use. No further pre-treatment was used. The TTBA source was held at 30°C at which temperature it has a

suitable vapour pressure (>1 Torr) for LPCVD. This produced growth rates upto 1.2 mh^{-1} at a substrate temperature of 400°C . Layer thickness was obtained using tallystep methods. A full summary of growth conditions is given in Table 1 below.

Table 1

Growth conditions used to deposit aluminium from TTBA

10	Cell pressure	4.56 Torr
	Substrates	Single crystal Si(111)
	TTBA source temperature	30°C
	N_2 carrier gas flow	1.0S - 3.0 SCCM
	Growth Temperature	$300 - 400^{\circ}\text{C}$
15	Maximum growth rates	1.5 mh^{-1} at 400°C

The aluminium films were characterised initially by dissolution in hydrochloric acid and metals analysis for by inductively coupled mass spectrometry (ICP-MS) which showed them to be aluminium $> 99\%$ purity on a metals basis.

Aluminium films were deposited from TTBA in the temperature range of from $300 - 400^{\circ}\text{C}$ and were matt grey with only a low reflectivity (typically 30% at 633nm). This may be attributed to rough surface morphology which has frequently been observed in films deposited using TIBA unless pre-treatment with TiCl_4 is employed.

The aluminium films produced from TTBA were found

to be conducting.

The adhesive properties of films grown on Si(111) at 400°C was also excellent and in the "Scotch tape" test the films remained intact as the tape was peeled
5 away from the aluminium film.

The use of trialkylaluminium precursors for deposition of aluminium raises concern about incorporation of carbon in the deposited film especially at the relatively high substrate temperatures
10 used in this Example. However, the results of Auger electron analysis, as shown in Table 2 below indicate that only trace carbon and oxygen are present in aluminium films grown at 400°C using TTBA.

For comparison the conventional precursor TIBA
15 was used to deposit an aluminium film under identical conditions to those shown in Table 1 above. Auger analysis of this layer is given in Table 2 below and shows it to be of lower purity than the layer from TTBA, containing higher levels of carbon and of oxygen.
20 Further analysis of separate aluminium films by secondary ion mass spectroscopy confirmed that carbon levels were at least a factor of three lower in aluminium films grown using TTBA compared with those grown using TIBA.

25

Table 2

Auger electron spectral analysis of aluminium

films grown at 400°C on Si(111) using TTBA and TIBA.

Atomic Composition %

	Film Precursor	Al	C	O
5	TTBA	98.2	0.7	1.1
	TIBA	84.5	3.1	12.4

* Sub-surface information (2000 Å or below) obtained by combining AES with sequential ion bombardment.

Levels of oxygen in aluminium films grown using
10 TTBA were found to be lower than those grown using TIBA.
This may reflect a reduced tendency for oxygen to be
entrained in the sterically bulky and rigid TTBA
molecule. The presence of oxygen at all in the TTBA-
grown film may be attributed to the use of a simple CVD
15 reactor from which rigorous exclusion of trace oxygen
was not possible.

CLAIMS

1. A method of depositing a Group III A metal film on a substrate comprising the steps of contacting the substrate with a Group IIIA metal precursor and
5 treating the precursor to decompose leaving the Group IIIA metal deposited in the substrate, wherein the precursor is the tritertiarybutyl compound of the Group IIIA metal.
2. A method as claimed in claim 1, wherein the Group
10 IIIA metal is selected from aluminium, gallium and indium.
3. A method as claimed in claim 1 or 2, wherein the precursor is delivered to the substrate as a vapour phase and is pyrolyzed on the substrate.
- 15 4. A method as claimed in claim 1 or 2, wherein the precursor is in liquid form and the substrate is coated therewith before heating to pyrolyze the precursor.
5. A method as claimed in any one of claims 1 to 4, wherein the substrate is heated to a temperature in the
20 range of 150 to 400°C.
6. A method as claimed in any one of claims 1 to 5, wherein the substrate is silicon or polyamide.
7. A method as claimed in any one of claims 1 to 6, wherein a Group IIIA/silicon alloy is formed by
25 treatment of the precursor with a silicon precursor also

deposited on the substrate.

8. A method as claimed in claim 7, wherein the silicon precursor is SiH_4 .

9. A method as claimed in any one of claims 1 to 6,
5 wherein a Group III/V alloy is produced by treatment of the Group IIIA precursor with a Group V precursor also deposited on the substrate.

10. A method as claimed in claim 9, wherein the alloy produced is selected from AlGaAs, AlInAs and AlSb.

10 11. A method of depositing a Group IIIA metal film on a substrate substantially as hereinbefore described with reference to the foregoing Example.

12. A substrate having a Group IIIA metal layer deposited thereon by a method as claimed in any one of
15 claims 1 to 11.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 94/01654

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C23C 16/18, C23C 16/20, C23C 18/08, C23C 18/10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SURFACE SCIENCE, Volume 278, No 1-2, 1992, E.T. FitzGerald et al, "Comparative studies of the thermal decomposition of tritertiarybutylgallium and tri-isobutylgallium on GaAs(100)", page 111 - page 120, see page 120, column 1, line 13 - line 42; abstract	1-3,12
Y	abstract	4-7,9,10

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF CRYSTAL GROWTH, Volume 120, No 1-4, 1992, J.S. Foord et al, "Applications of MBMS and surface spectroscopic techniques in the study of reaction mechanisms in CBE; investigations of the reactivity of tritertiarybutylgallium and triisobutylgallium as alternative precursors....", page 103 - page 113, see page 85, column 1, line 1 - line 31; abstract	1-3,12
Y	abstract	4-7,9,10
	--	
X	JOURNAL OF CRYSTAL GROWTH, Volume 124, No 1-4, 1992, A.C. Jones et al, "New metalorganic gallium precursors for the growth of GaAs and AlGaAs by CBE", page 81 - page 87, see page 106, column 1, line 36 - line 38; page 111, column 2, line 21 - page 112, column 1, line 2; abstract	1-3,12
Y	abstract	4-7,9,10
	--	
P,X	JOURNAL OF CRYSTAL GROWTH, Volume 135, No 1-2, 1994, A.C. Jones et al, "Growth of aluminium films by low pressure chemical vapour deposition using tritertiarybutylaluminium", page 285 - page 289, see page 286, column 1, line 16 - line 29; abstract	1-3,5,6,11,12
P,Y	abstract	4,7-10
	--	
Y	GB, A, 1320098 (CONTINENTAL OIL COMPANY), 13 June 1973 (13.06.73), page 1, column 2, line 94 - page 2, column 1, line 1; page 2, column 1, line 60 - column 2, line 2, figure 1, claims 1,8,9	4,5
	--	
Y	US, A, 4328261 (RUDOLF A. H. HEINECKE ET AL), 4 May 1982 (04.05.82), claims 1,14, abstract	5-7
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 94/01654

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE, A1, 3631469 (MERCK PATENT GMBH), 17 March 1988 (17.03.88), column 2, line 2 - line 9 -----	9-10

INTERNATIONAL SEARCH REPORT
Information on patent family members

01/10/94

International application No.

PCT/GB 94/01654

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB-A-	1320098	13/06/73	DE-A-	2116546	28/10/71
			FR-A-	2085871	31/12/71
			US-A-	3620189	16/11/71
<hr/>					
US-A-	4328261	04/05/82	DE-A-	2944500	29/05/80
			FR-A,B-	2441271	06/06/80
			GB-A,B-	2038883	30/07/80
			GB-A,B-	2041983	17/09/80
			DE-A-	3040693	27/05/81
			FR-A,B-	2469467	22/05/81
			JP-A-	56083026	07/07/81
<hr/>					
DE-A1-	3631469	17/03/88	DE-A-	3775311	30/01/92
			EP-A,B-	0260534	23/03/88
			JP-A-	63083092	13/04/88
			US-A-	4880492	14/11/89
			US-A-	5112432	12/05/92
			US-A-	5149853	22/09/92
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